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Embedding Au nanoclusters into the pores of carboxylated COF for efficient photocatalytic production of hydrogen peroxide

Qigao Shang [a], Yanyang Liu [a], Jing Ai [a], Ying Yan [a], Xiaofang Yang [b], Dongsheng Wang [c], Guiying Liao [a,*]

[a] Faculty of Materials Science and Chemistry, China University of Geosciences, Wuhan 430074, P. R. China.

[b] State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

[c] College of Environmental & Resource Sciences, Zhejiang University, Hangzhou 310058, 14 China

Corresponding authors:

(Guiying Liao) E-mail: liaogy@cug.edu.cn

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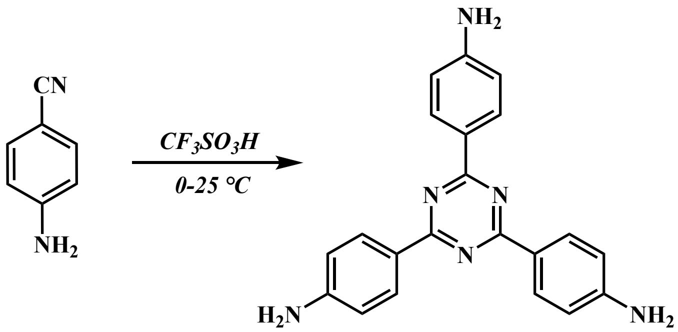
Physical Measurements

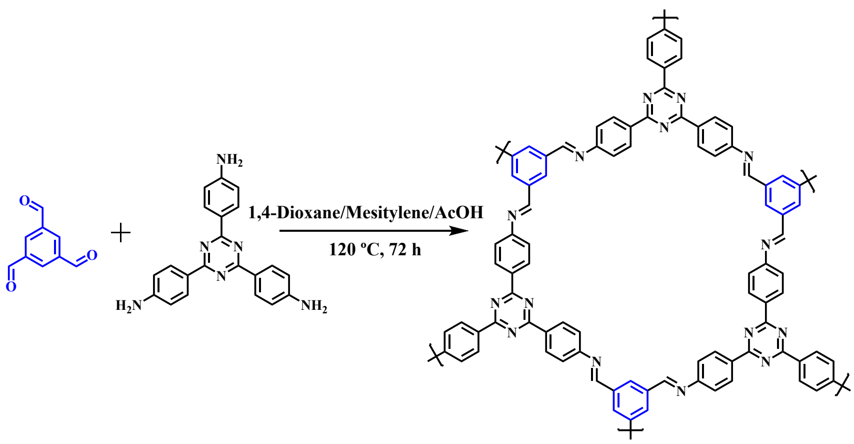
Fourier transform infrared **(FT-IR)** spectra were observed on a Thermal Nicolet iS50 spectrometer using powder samples embedded in potassium bromide (KBr) pellets the solid state ^{13}C cross-polarization magic angle spinning **(CP/MAS) NMR** spectra were taken in a Bruker 300 MHz NMR spectrometer. Powder X-ray diffraction **(XRD)** was performed on a Bruker D8 Advance X-ray diffractometer with Ni-filtered Cu Kα radiation (λ= 0.154178 nm) at 40 kV ranging from 3° to 90°. The morphologies of the samples were investigated by field emission scanning electron microscopy (**SEM**, SU-70, Hitachi). The high-resolution transmission electron microscopy **(HRTEM)** images were performed on JEM 2100 electron microscope (JEOL, Japan). The UV-vis diffuse reflectance spectra **(UV-vis DRS)** of the samples were measured on a UV-visible spectrophotometer (UV-2600, Shimadzu Corp., Japan), with an integrating sphere attachment and BaSO4 reference. X-ray photoelectron spectroscopy **(XPS)** measurements were tested on an Axis Ultra DLD using C1s (284.8 eV) as a reference to correct the binding energy. The Brunauer-Emmett-Teller **(BET)** surface areas and nitrogen adsorption/desorption isotherms were measured at 77 K using Micromeritics ASAP2460 equipment. The pore size distribution was derived from the adsorption branch of N_2 isotherms using the nonlocal density functional theory (NLDFT) method, and the total pore volume was evaluated through nitrogen uptake at P/P0 of 0.99. Electron paramagnetic spectroscopy **(EPR)** were measured on a Bruker EMX plus model spectrometer.

Materials

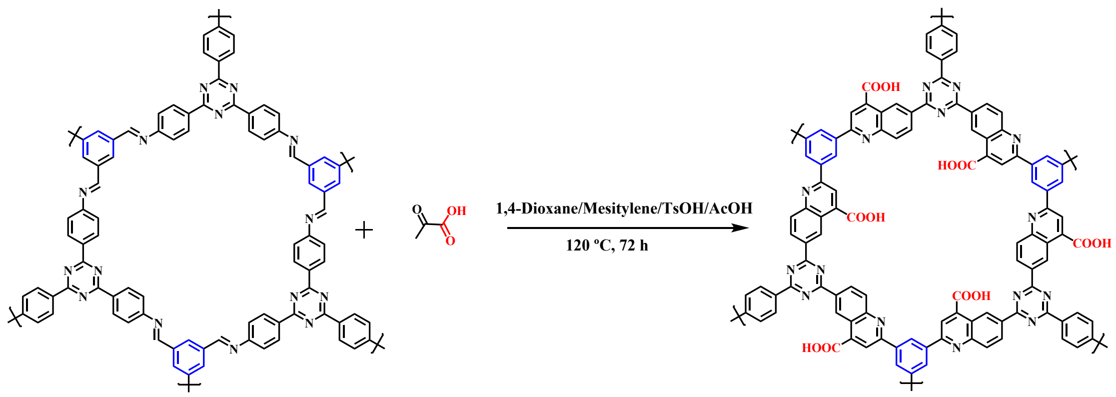
4-Aminobenzonitrile, Trifluoromethanesulfonic acid, 1,3,5-Triformylbenzene, Mesitylene, Pyruvic acid, Glutathione (GSH), were purchased from Shanghai Aladdin Chemistry Co. 1,4-Dioxane, Acetic Acid, p-toluenesulfonic Acid, $HAuCl_4 \cdot 3H_2O$, Ethanol, Methanol, Benzyl alcohol (BA), propan-2-ol (IPA) and tetrahydrofuran (THF) were purchased from Sinopharm Chemical Reagent Co., Ltd.



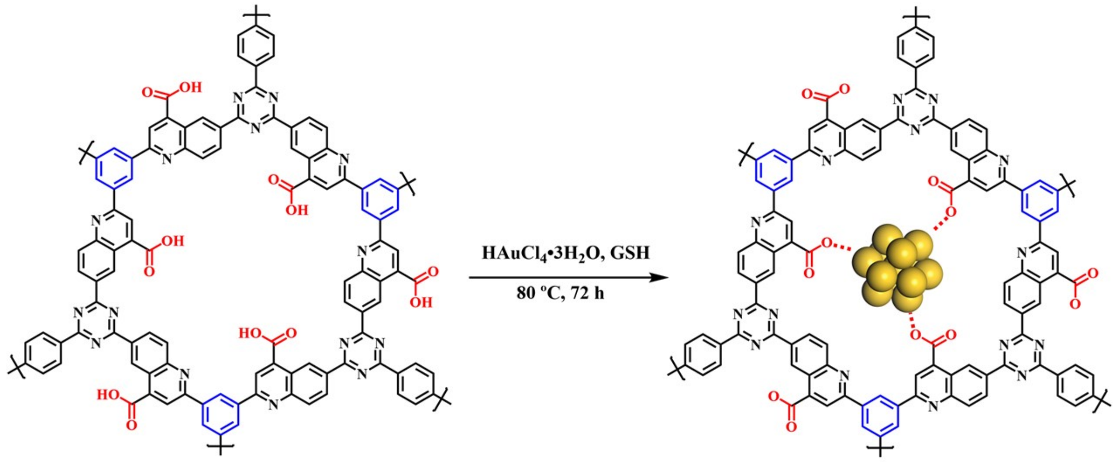
Scheme S1. Synthesis of TAPT monomer.



Scheme S2. Synthesis of T-COF



Scheme S3. Synthesis of COF-COOH



Scheme S4. Synthesis of Au@COF

Iodometry:

The amount of H_2O_2 was determined by iodometry. Typically, 1 mL of 0.1 M $C_8H_5KO_4$ solution and 1 mL of 0.4 M KI solution were added into 2 mL of the reaction solution and kept for 30min. H_2O_2 can react with I^- under acidic conditions to form I^{3-} ($H_2O_2 + 3I^- + 2H^+ \rightarrow I^{3-} + 2H_2O$). The amount of I^{3-} was determined by measuring the absorbance at 350 nm by UV-vis spectroscopy, from which the total amount of H_2O_2 produced during the photocatalytic reaction can be calculated, **Figure S1** shows the standard curve of H_2O_2.

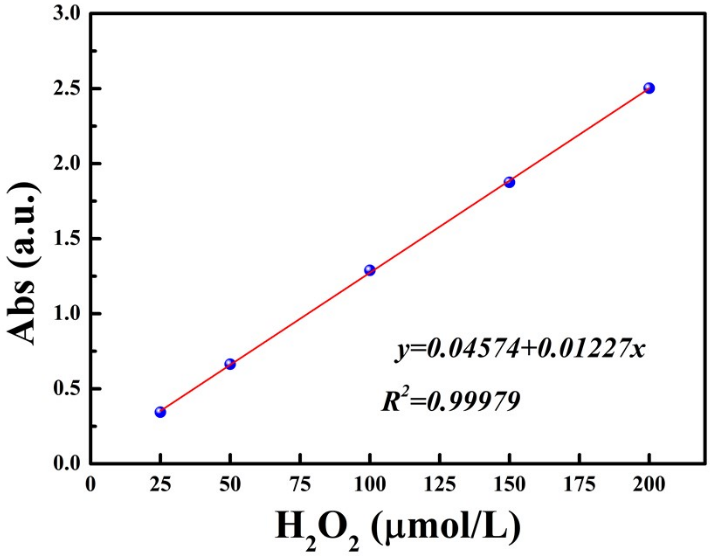


Figure S1. The linear fitting formula of standard H_2O_2 concentration.

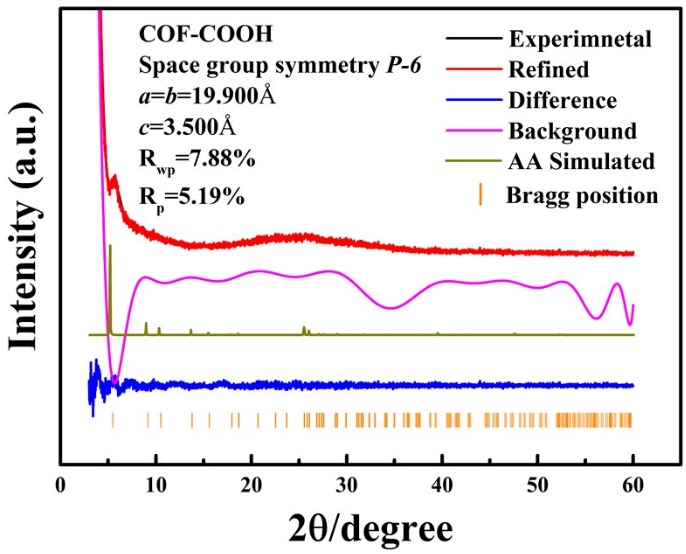


Figure S2. Experimental and simulated PXRD patterns of COF-COOH.

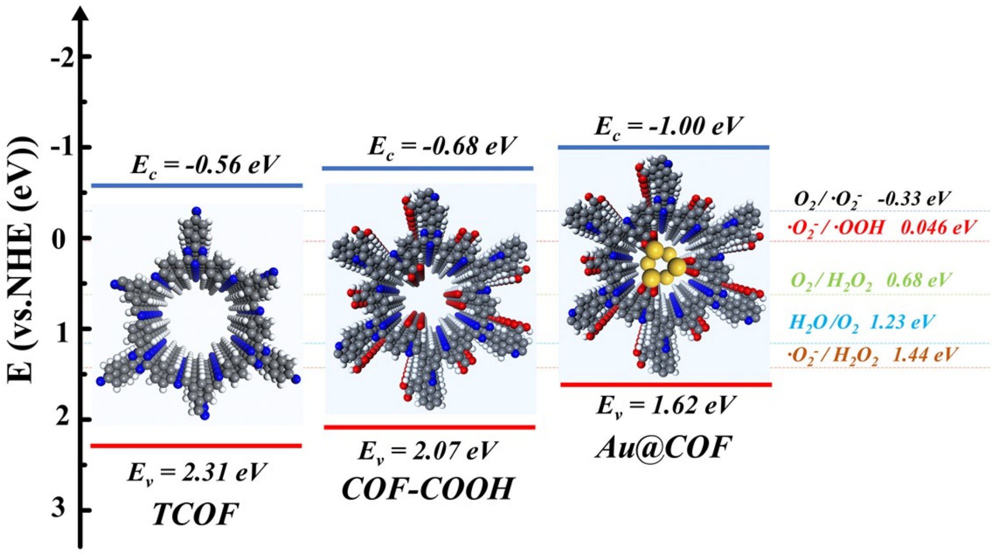


Figure S3. Band structure diagram of TCOF, COF-COOH and Au@COF.

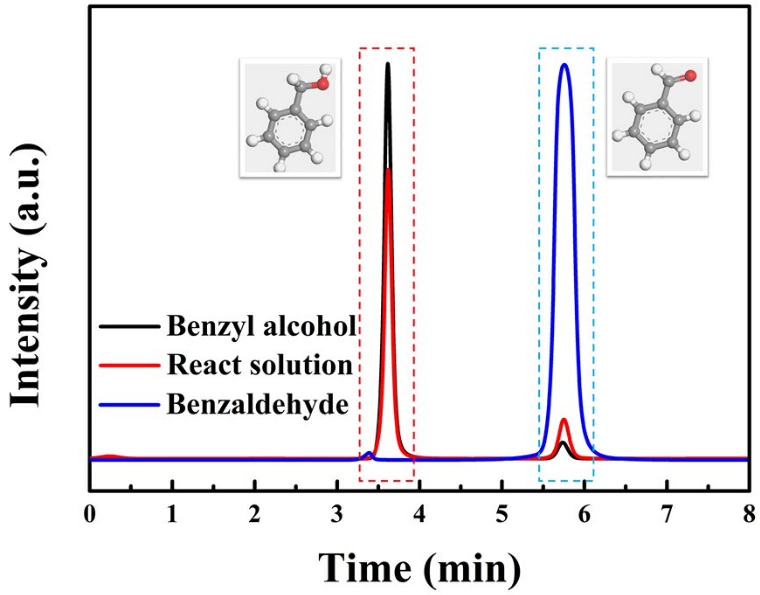


Figure S4. The HPLC of benzyl alcohol, reaction solution and benzaldehyde.

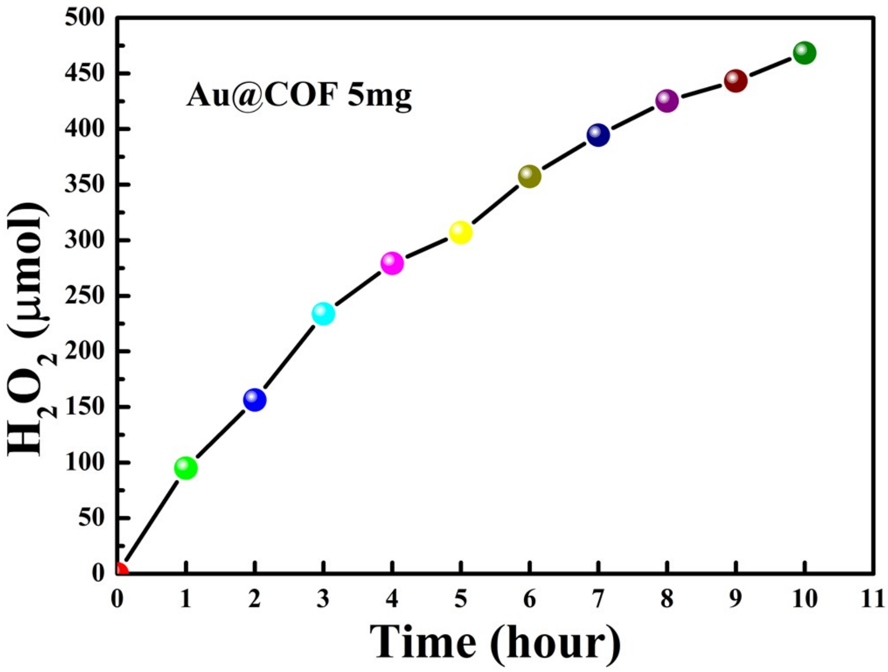


Figure S5. Au@COF photocatalytic H_2O_2 production performance

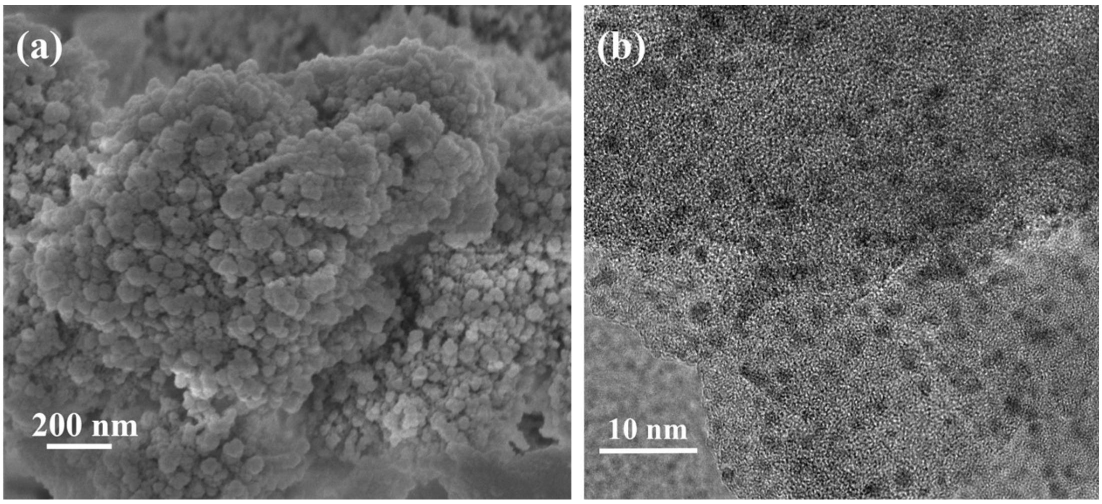


Figure S6. (a) SEM and (b) TEM of Au@COF after five cycles of photocatalysis

Table S1. Atomistic coordinates for the Pawley-refined COF-COOH.

Eclipsed mode Space group symmetry *p-6*, $a = b$ = 19.900 Å, c = 3.500 Å, $\alpha = \gamma$ = 90°, β = 120°, R_p = 5.19% and R_{wp} = 7.18%			
Atom	x	y	z
C1	0.00391	0.00391	-0.0000
C2	0.08700	0.03511	-0.0000
C3	0.17572	0.07110	-0.0000
C4	0.21195	0.01854	-0.0000
C5	0.22807	0.15987	-0.0000
C6	0.30078	0.05496	-0.0000
C7	0.31700	0.19651	-0.0000
C8	0.35331	0.14385	-0.0000
C9	0.37017	0.28543	-0.0000
C10	0.45868	0.32006	-0.0000
C11	0.49318	0.26601	-0.0000
C12	0.57804	0.29833	-0.0000
C13	0.61300	0.24465	-0.0000
H14	0.04725	0.22030	-0.0000
H15	0.20075	0.19826	-0.0000
H16	0.32772	0.01611	-0.0000
H17	0.45252	0.44274	-0.0000
H18	0.49869	0.38569	-0.0000
H19	0.57328	0.17897	-0.0000
N20	0.03515	0.94809	-0.0000
N21	0.44046	0.17901	-0.0000
O22	0.03626	0.60925	-0.0000
O23	0.05863	0.75014	-0.0000

Table S2. summarized the performance of Au@COF compared to various photocatalysts reported in recent years for the photocatalytic generation of H_2O_2.

Material	*solution*	*Photocatalyst Concentration mL/mg*	*H_2O_2 yields/ µmolg^{-1}h^{-1}*	*H_2O_2 yields/ µmolh^{-1}*	*Irradiation conditions /nm*	*Ref.*
COF-COOH	10 vol% BA	50/5	**9479.60**	**47.40**	Simulated sunlight	**This work**
Au@COF	10 vol% BA	50/5	**18933.58**	**94.67**		
1H-COF	10 vol% IPA	30/ 30	1483.33	44.50	λ≥420	S1
Bpy-TAPT	Pure water	30/5	4038.00	20.19	λ≥420	S2
ZIF-8/C_3N_4	Pure water	15/10	2641.00	26.41	420≤ λ ≤ 700	S3
COF-NUST-16	10 vol% EtOH	50/5	1081.00	5.40	λ≥420	S4
Py-Da-COF	10 vol% BA	5/5	3670.00	18.35	λ≥420	S5
EBA-COF	10 vol% BA	2.5/10	2550.00	25.50	λ=420	S6
COF-TAPB-BPDA	5 vol% BA	25/5	1240.00	6.20	λ≥420	S7
TPB-DMTP-COF	Pure water	50/10	2882.00	28.82	λ≥420	S8
Bpt-CTF	Pure water	50/10	3268.10	32.68	350≤ λ ≤ 780	S9
TF_{50}-COF	10 vol% EtOH	50/5	1739.00	8.70	λ≥400	S10
N0-COF	Pure water	20/10	1570.00	15.70	495 nm LED	S11
sonoCOF-F2	10 vol% BA	5/3	2422.22	7.27	λ≥420	S12
DE7-M	$Sc(NO_3)_3$ 150 mM	3/5	2216.67	11.08	λ≥420	S13
Nv-C≡N-CN	Pure water	20/20	3930.00	78.60	λ≥420	S14
$Cu_2(OH)PO_4$/g-C_3N_4	Pure water	200/200	1200.00	240.00	Simulated sunlight	S15
Au/ZnO	4vol%EtOH	200/200	1525.00	305.00	UV light	S16
$ZnIn_2S_4/TiO_2$	Pure water	50/30	1530.59	45.92	400 nm ≤ λ ≤ 760	S17
Ni-CAT-CN	Pure water	15/10	1801.05	18.01	λ≥420	S18
ZnO@PDA	Pure water	50/20	2528.50	50.57	300 W Xenon lamp	S19
ZnO/g-C_3N_4	10 vol% EtOH	50/20	3860.00	77.20	λ≥ 350	S20
Pt/TiO_2	Pure water	20/1	5096.00	5.10	λ≥300	S21
ZnO/WO_3	10 vol% EtOH	50/50	6788.00	339.40	300 ≤ λ ≤ 700	S22
OPA/Zr_{100-x}Tix-MOF	71.4 vol% BA	7/5	13580.00	67.9	λ≥420	S23
HTNT-CD	Pure water	15/20	4235.00	84.7	λ≥365	S24
MIL-125-PDI	80/ CH_3CN	5/5	4800.00	24.00	λ≥420	S25

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